ZnSe nanorods as a visible-light-absorber for photocatalytic and photoelectrochemical H_2 evolution from water

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Abstract: *A precious metal- and Cd-free photocatalyst system for efficient H_2 evolution from water with a performance comparable to Cd-based quantum dots is presented. Rod-shaped ZnSe nanocrystals (nanorods, NRs) with a $Ni(BF_4)_2$ co-catalyst suspended in aqueous ascorbic acid evolve H_2 with up to 54±2 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} under visible light illumination (λ > 400 nm, AM 1.5G, 100 mW cm^{-2}), and 50±4 % quantum yield (λ = 400 nm). Under full-spectrum simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}), up to 149±22 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} are generated. Significant photocorrosion was not observed within 40 h and activity was even observed without added co-catalyst. The ZnSe NRs can also be employed to construct an inexpensive Delafossite-based photocathode, which does not rely on a sacrificial electron donor. Immobilized ZnSe-NRs on $CuCrO_2$ generate photocurrents of ~10 μA cm^{-2} in aqueous electrolyte solution (pH 5.5), with a photocurrent onset potential at ~+0.75 V vs. RHE. This work establishes ZnSe as a state-of-the-art light-absorber for photocatalytic and photoelectrochemical H_2 generation.*

Artificial photosynthesis, in which solar energy is stored in chemical fuels is a promising strategy for overcoming the temporal mismatch between renewable energy supply and demand.[1] H_2 is the most prominent example of a solar fuel as it can be generated by photoreduction of aqueous protons by a broad range of photocatalysts.[2] Among the most active materials are chalcogenide nanocrystals based on CdS and CdSe.[3] Despite the remarkable activities and stabilities shown by these materials,[4] the toxicity and carcinogenic nature of cadmium represents a considerable obstacle for their widespread application. Carbon-based materials, such as carbon nitride,[5] carbon dots,[6] and conjugated organic polymers[7] have recently been introduced as benign alternatives. While these materials are inexpensive and non-toxic, their performances have yet to match those of Cd-based photocatalysts to achieve high quantum yields for aqueous H_2 production without precious and carcinogenic metals.

Here, we report ZnSe nanorods (NRs) as an inexpensive, Cd-free light-absorber for efficient H_2 evolution under visible-light irradiation. The ZnSe NRs exhibit activity approaching that of Cd-based materials, even without an added co-catalyst. Furthermore, we demonstrate that the superior activity of suspended ZnSe nanocrystals under sacrificial conditions can be translated to heterogeneous conditions by assembling a simple, precious-metal-free photoelectrode from ZnSe nanocrystals immobilized on p-type $CuCrO_2$.

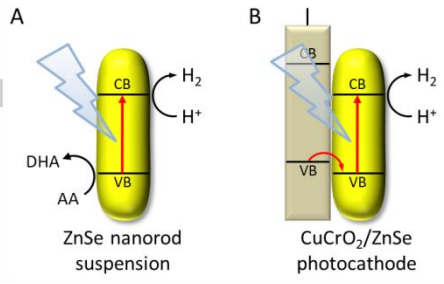

Figure 1. Schematic representation of the reported ZnSe nanorod photocatalyst system and its application for the construction of a noble-metal-free photocathode (CB = conduction band, VB = valence band).

ZnSe is a stable and inexpensive semiconductor with a direct bulk band gap of 2.7 eV,[8] which enables absorption of near-UV and some visible light. The conduction band (CB) is located at around –1.1 V *vs.* NHE (pH 0),[9] providing ample driving force for the reduction of aqueous protons. Despite these favorable properties, ZnSe has received surprisingly little attention for solar fuel generation, unlike its cadmium analogues CdS and CdSe.[10] Domen and co-workers reported ZnSe-copper indium gallium selenide (CIGS) solid solution-based photocathodes for H_2 evolution[11] with photocurrents up to 12 mA cm^{-2} at 0 V vs. RHE and onset potentials of +0.89 V vs. RHE.[11b] However, the complex photocathode assembly required a CdS extraction layer and a Pt proton reduction catalyst. While a number of reports have demonstrated the application of ZnSe-based nanomaterials for photocatalytic dye degradation,[12] and water oxidation,[13] only a few examples of Cd-free ZnSe particles for photocatalytic H_2 generation have been reported, all of which show low activity.[14]

We prepared ZnSe NRs by injecting trioctylphosphine/Se into an octadecane solution of zinc stearate at 300 °C, followed by a 25 min growth period.[15] Surface modification of as-prepared stearate-capped ZnSe NRs (ZnSe-St) was achieved by ligand exchange with mercaptopropionic acid to give water-soluble NRs (ZnSe-MPA), and by reactive ligand removal with $[Me_3O][BF_4]$ to give ligand-free NRs (ZnSe-BF_4).[16] Independent of the surface capping, the NRs are 5.2±0.6 nm in diameter and 30.0±4.8 nm long (aspect ratio 5.8±0.9), as determined from transmission electron microscopy (TEM, Fig. S1). Powder X-ray diffraction (Fig. S1F) shows that the ZnSe NRs are obtained as a mixture of the zinc blende and wurtzite polymorphs, as has

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been previously observed with ZnSe nanorods synthesized by hot injection.[17] ZnSe NRs show UV-visible light absorption up to ~440 nm (Fig. S2A) and two emission maxima separated by 0.097 eV in their photoluminescence (PL) spectra that can be attributed to differences in the band gaps of the two ZnSe polymorphs (Fig. S2B).[18] Additional emissions at longer wavelengths likely result from trap states as previously observed with ZnSe nanocrystals.[16a] PL is reductively quenched by adding ascorbic acid (AA, Fig. S2C-D).

Fig. 2 shows that ZnSe NRs are highly active photocatalysts for the reduction of aqueous protons to H_2 under visible-light irradiation (AM 1.5G, λ>400 nm, 100 mW cm^{-2}) in the presence of AA. Under optimized conditions (pH 4.5, 0.4 M AA, 50 mg L^{-1} ZnSe, see Table S1 and Fig. S3 for optimization details), ZnSe-BF_4 produced up to 33.6±2.0 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} (Fig. 2A). To further enhance the photocatalytic activity of ZnSe NRs, $Fe(BF_4)_2$, $Co(BF_4)_2$, $Ni(BF_4)_2$ and K_2PtCl_4 were tested as co-catalysts (Fig. 2B). Ni showed the highest performance increase to 54.3±1.9 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} at 20 µM, whereas K_2PtCl_4 quenched the photocatalytic activity almost completely. We speculate that ligand-free particles suppress the deposition of Pt particles on the ZnSe surface, as previously observed with ligand-free CdS;[19] pre-formed Pt nanoparticles showed a higher activity, but still lower than without co-catalyst. Under the same conditions, ligand-capped ZnSe-MPA and ZnSe-St NRs showed a lower H_2 generation activity of 45.9±1.4 and 12.1±2.7 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1}, respectively (Fig. 2B). This observation agrees with our previous studies, demonstrating enhanced HER activity of CdS nanocrystals upon ligand removal.[20] Under full-spectrum simulated solar irradiation (AM 1.5G, 100 mW cm^{-2}), ZnSe-BF_4 generates up to 149±22 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} and 95±27 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1} in the presence and absence of $Ni(BF_4)_2$, respectively (Fig. 2C). The internal quantum yield (IQE) under 400 nm monochromatic light was 50.2±3.6 % (35.9±2.6 % external quantum yield, EQE, Table S2).

Long-term experiments using ZnSe-BF_4 showed that H_2 production is sustained over more than 40 h with a gradual decrease in rate (Fig. 2D). This decreasing activity is likely due to accumulation of dehydroascorbic acid (DHA) in solution. Photodegradation of ZnSe is only marginal as separating ZnSe-BF_4 NRs after 20 h and re-dispersing them in a fresh AA solution largely restored activity (some material is lost during separation). In contrast, adding fresh ZnSe NRs had no effect on the activity (Fig. S4). Previous work has shown that the AA oxidation product DHA can inhibit photocatalytic H_2 production.[21] UV-vis spectra before and after prolonged irradiation show no degradation apart from an increase in scattering resulting from particle aggregation (Fig. S5). Post-catalysis TEM confirms the formation of aggregates with aspherical nanocrystalline features (Fig. S6). Inductively-coupled plasma optical emission spectroscopy (ICP-OES) of ZnSe-BF_4/Ni isolated after 3 h irradiation showed incorporation of 8.5±2.3 Ni atoms per ZnSe NR (<1 % of total added Ni), suggesting *in-situ* formation of a heterogeneous Ni-based catalyst on the NR surface.[22] No H_2 was generated without ZnSe, in the dark or without electron donor (Table S3).

These data demonstrate that ZnSe-BF_4 NRs are a highly efficient and stable light-absorber for aqueous H_2 production, considerably outperforming previous Cd-free ZnSe photocatalysts, despite its blue-shifted absorption spectrum compared to CdS. Previous reports have shown that s Pt/ZnO-ZnSe nanocomposite generated 3 $mmol_{H2}$ g^{-1} h^{-1} under UV irradiation with 2.54 % EQE,[14a] and CoP-decorated ZnSe nanobelts produced < 1 $mmol_{H2}$ g^{-1} h^{-1} under visible-light irradiation.[14b] However, the photocatalytic activities of ZnSe-BF_4 (33.6±2.0 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1}, 25.9±1.2 % EQE) and ZnSe-BF_4/Ni (54.3±1.9 $mmol_{H2}$ g_{ZnSe}^{-1} h^{-1}, 35.9±2.6 % EQE) approach those of Cd-based photocatalysts,[23] such as $Cd_{0.25}Zn_{0.75}Se$/CoP (45.1 $mmol_{H2}$ g^{-1} h^{-1}).[14b] CdSe quantum dots (QDs) combined with a Ni catalyst were shown to produce H_2 with an IQE of 36±10 %.[24] Higher performances were reported for CdS with different co-catalysts[25] such as MoS_2 (96.7 $mmol_{H2}$ g^{-1} h^{-1}, 46.9 % EQE),[25a] Ni_2P (1,200 mol_{H2} g^{-1} h^{-1}, 41 % EQE)[25b] and Pt/PdS (29.2 $mmol_{H2}$ g^{-1} h^{-1}, 93 % EQE).[25c] Without co-catalyst, up to 41 mol_{H2} g^{-1} h^{-1}[26] and 2.8 % EQE[27] were reported for CdS and 239 $mmol_{H2}$ g^{-1} h^{-1}[28] and 65.7 % EQE[29] for $Cd_xZn_{1-x}S$. Cd-free alternatives such as $CuInS_2$-ZnS,[30] carbon nitride,[31] conjugated polymers,[32] triazine frameworks,[33] and polymer dots[34] generally show much lower activities, although a recently reported NaCl/KCl-treated carbon nitride/Pt material achieved up to 60 % EQE.[35]

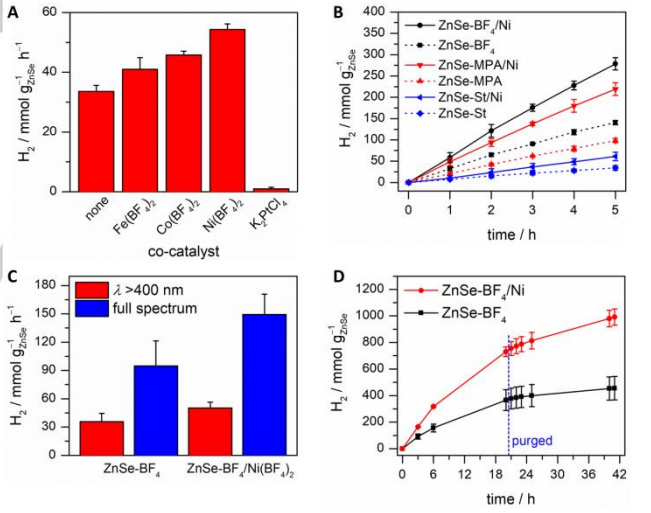

Figure 2. Photocatalytic H_2 generation using aqueous ZnSe-NRs. (A) Ligand-free ZnSe-NRs in the presence of different co-catalysts (3 h irradiation). (B) Effect of the NR capping ligand. (C) ZnSe-BF_4 under different irradiation spectra (1 h irradiation). (D) Long-term activity of ZnSe-BF_4, where photoreactor was purged with N_2 after 20 h, cumulative H_2 is shown. Conditions unless otherwise stated: 50 mg L^{-1} ZnSe-NRs, 0.4 M AA, pH 4.5, 20 µM $Ni(BF_4)_2$, 25 °C, 100 mW cm^{-2}, AM 1.5G, λ >400 nm. Lines between data points have been added to guide the eye.

Having established good performance and stability of ZnSe nanorods for photocatalytic H_2 production, even in the absence of added co-catalyst, we aimed to eliminate the sacrificial electron donor AA. The production of low-value H_2 gas at the expense of a sacrificial electron donor is not sustainable unless the electron donor is freely available, for example by photoreforming waste.[19, 36] Instead, a nanocrystal-sensitized photocathode can be assembled, where the nanocrystal provides electrons for photocatalysis, and a p-type semiconductor accepts photogenerated holes, replacing the electron donor. Such systems enable overall water splitting through coupling with a photoanode for water oxidation.[37]

To this end, we immobilized ZnSe-BF_4 NRs on a $CuCrO_2$ electrode. $CuCrO_2$ is a wide-bandgap semiconductor (E_g~3.1 eV), which crystallizes in a Delafossite-type structure. Previous work has shown that modification of $CuCrO_2$ with an organic dye and a nickel bis(diphosphine) catalyst enabled visible light driven proton reduction in aqueous solution.[38] The characteristic high hole mobility, p-type conductivity, and straightforward synthesis from abundant materials using solution processing techniques, position $CuCrO_2$ as a suitable candidate for coupling with ZnSe in a hydrogen-generating photocathode.

ZnSe nanorods were immobilized by drop casting (8 µL cm^{-2}, 1.66 mg mL^{-1}, acetonitrile) directly on $CuCrO_2$ electrodes (thickness approx. 300 nm, Fig. S7; 13.4 µg ZnSe cm^{-2}), with EDX spectra confirming an even distribution over the electrode surface (Fig. S8). UV-vis spectra of ZnSe-modified $CuCrO_2$ feature the characteristic absorptions of both $CuCrO_2$ and ZnSe (Fig. S9). Linear sweep voltammograms and chrono-amperograms of ZnSe-modified electrodes show enhanced photocurrents over the bare $CuCrO_2$ electrode with an onset potential of approximately +0.75 V vs. RHE (Fig. 3), indicating the ability of photoexcited ZnSe nanorods to inject holes ($E_{VB,\ ZnSe}$ = 1.6 V vs. RHE) into the valence band of $CuCrO_2$ ($E_{VB,\ CuCrO2}$ = 1.0 V vs. RHE).[38] Controlled potential photoelectrolysis (CPPE, Fig. S10) confirmed that the highly reducing CB_{ZnSe} electrons are used to reduce aqueous protons to H_2. CPPE with a $CuCrO_2$|ZnSe electrode maintained at E_{app} = 0 V vs. RHE and illuminated from the front side (100 mW cm^{-2}, AM 1.5G, λ > 400 nm) produced 35±7 nmol H_2 over the course of 4 h with a Faradaic efficiency (FE) of 7±2 % (Table S5). Bare $CuCrO_2$ produced no detectable H_2, confirming the essential role of ZnSe in this system. The high dark current, as previously reported for $CuCrO_2$,[38] and dissolved H_2 that is not sufficiently accounted for in low current-generating systems,[39] both contribute to the modest FE. Adding Ni^{2+} as a co-catalyst increases the overall H_2 production yield, corresponding well with photocatalysis results (Fig. S11, Table S5). Incident photon-to-current efficiency measurements showed an increased current in the 400-440 nm region for $CuCrO_2$|ZnSe electrodes compared to bare $CuCrO_2$ confirming the role of ZnSe-NRs in this photocathode (Fig. S12).

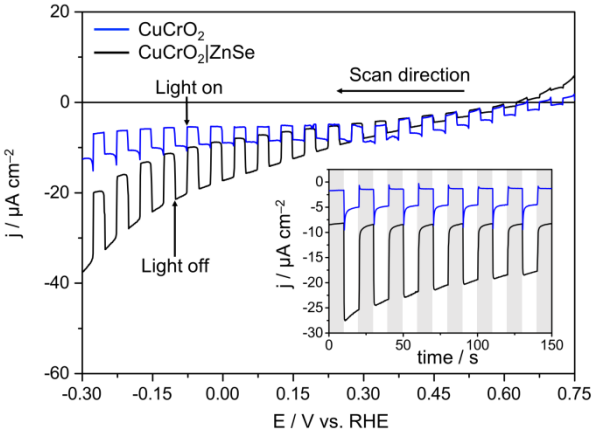

Figure 3. Linear sweep voltammograms under chopped light illumination for $CuCrO_2$ (blue) and $CuCrO_2$|ZnSe (black) electrodes, and chronoamperograms (inset) of these electrodes held at E_{app} = 0 V vs. RHE. Shading indicates dark chops. Conditions: Aq. Na_2SO_4 (0.1 M, pH 5.5), room temperature, 100 mW cm^{-2}, AM 1.5G, λ > 400 nm, scan rate 5 mV s^{-1}. The photocurrent density was adjusted for an electrode area of 0.25 cm^2.

H_2-generating QD-sensitized photocathodes in the absence of a co-catalyst have reported photocurrents of –60 µA cm^{-2} at 0.3 V vs. RHE with mercaptoacetic acid modified CdSe on NiO,[40] and –180 µA cm^{-2} at 0.5 V vs. RHE using a phenothiazine hole-accepting ligand with CdSe on NiO were observed.[41] $CuCrO_2$|ZnSe photoelectrodes generated –10 µA cm^{-2} at 0 V vs. RHE, comparable to photocurrents observed with a molecular dye/catalyst assembly.[38] The low photocurrent can be partly attributed of low light absorption, but the dominant limiting factor is likely a non-ideal interface between $CuCrO_2$ and ZnSe NRs. This results in high charge recombination, limiting the number of electrons available for catalysis. Adding a HER co-catalyst therefore only results in a small activity enhancement. Although this performance does not yet match that of the corresponding Cd-based systems, it does demonstrate that the ZnSe NR photocatalyst can operate in the absence of a sacrificial reagent and in a photoelectrochemical cell. We expect future improvements for the integration of ZnSe into electrodes from $CuCrO_2$ nanostructuring and ligand engineering to improve the $CuCrO_2$/ZnSe interface,[40-42] alternative assembly methods,[43] and integration of molecular catalysts,[44] especially for CO_2 reduction,[16a] making use of the highly reducing CB of ZnSe.

In summary, we have demonstrated that ZnSe nanorods are highly efficient light-absorbers for solar-driven H_2 production, even without added hydrogen-evolution co-catalyst. Their performance already approaches that of Cd-containing quantum dots without exhibiting their carcinogenicity, highlighting the potential of designing novel inorganic materials for efficient photocatalysis. We showed that the ZnSe nanorods can also be integrated into photoelectrochemical cells, which paves the way to closed-cycle solar fuel synthesis and we also envision its use in organic photoredox catalysis and photorefoming of waste and pollutants in future development.

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Keywords: photocatalysis • hydrogen • zinc selenide • delafossite • photocathode

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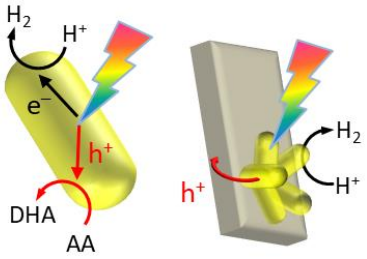
Entry for the Table of Contents

COMMUNICATION

Efficient visible-light driven H_2 generation was achieved using aqueous ZnSe nanorods as a stable, Cd-free light-absorber with benchmark activity of up to 150 mmol g^{-1} h^{-1} and 50 % quantum yield in suspension. A $CuCrO_2$|ZnSe photocathode was constructed for low-cost, co-catalyst free photoelectrochemical H_2 production.



ZnSe nanorod photocatalyst

$CuCrO_2$/ZnSe photocathode

*Moritz F. Kuehnel,‡ Charles E. Creissen,‡ Constantin D. Sahm,‡ Dominik Wielend, Anja Schlosser, Katherine L. Orchard, and Erwin Reisner**

Page No. – Page No.

ZnSe nanorods as a visible-light-absorber for photocatalytic and photoelectrochemical H_2 evolution from water